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Mutual toughening of vinylidene chloride and methyl methacrylate in network composites prepared via concentrated emulsion polymerization

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Polymer composites based on vinylidene chloride/methyl methacrylate (VDC/MMA) copolymer crosslinked with vinyl-terminated polycaprolactone (VTPCL) were prepared via a concentrated emulsion polymerization procedure. In that method, a partially polymerized solution of VDC, MMA and VTPCL in toluene, containing also an initiator, is dispersed at room temperature in a small amount of an aqueous solution of a surfactant. The concentrated emulsion thus generated is subjected to polymerization at 60°C. Compared to the polymerization in solution, which leads to a swollen bulk material, the concentrated emulsion polymerization provides latexes. The effects of the various constituents on the mechanical properties of the composites were studied via tensile testing. One concludes that there is mutual toughening between PVDC and PMMA, and that additional toughening is produced by the VTPCL. There is an optimum amount of VTPCL and an optimum weight ratio of VDC/MMA for which the toughness is maximum. Composites have also been prepared in which ethyl methacrylate or acrylonitrile replaced partially or completely MMA. Copyright © 1996 Elsevier Science Ltd.

(Keywords: composites; toughening; concentrated emulsion polymerization)

INTRODUCTION

The polymers based on vinylidene chloride (VDC) constitute an important family of materials. The most valuable property of poly(vinylidene chloride) (PVDC) and its copolymers is their low permeability to numerous gases and vapours. The most serious deficiency of PVDC is its thermal instability at the melt-processing temperature[1], which is why the homopolymer had no practical applications. The VDC polymers have been produced mainly in the form of copolymers, among which the following three types are important commercially: VDC/vinyl chloride copolymers, VDC/alkyl (meth)acrylate copolymers and VDC/acrylonitrile copolymers. They are widely used for films[2,3], containers and coatings[4,5].

Besides the above copolymers, it was noted[6–9] that tough plastics or flexible elastomers can also be prepared using VDC as a component. In the present paper, a novel network composite, based on VDC, methyl methacrylate (MMA) and vinyl-terminated polycaprolactone (VTPCL) was prepared, with VDC/MMA copolymer (chain A) crosslinked with polycaprolactone (PCL) (chain B). Such a network is called an AB network. By changing the contents of the constituents, the resulting material can be either tough or elastic. Since they are networks, these composites can be employed not only for packaging or coating, but also as energy or sound damping materials[10–12]. Furthermore, they possess improved anti-solvent and anti-thermal degradation properties. The composites were prepared via the concentrated emulsion polymerization method, which generates latexes. This is in contrast to the solution polymerization, which generates swollen bulk materials. In addition, the cross-linked structure being limited to each latex, the material can be more easily melt-processed than that prepared by solution polymerization.

The concentrated emulsion polymerization method[13,14] was recently developed by this group. A concentrated emulsion has the appearance of a paste, and differs from the conventional emulsion in that the volume fraction ϕ of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of monosize spheres). In the present work, a volume fraction $\phi = 0.85$ was employed. This is much higher than that in the conventional emulsion polymerizations for which ϕ is below 0.57 (ref. 15). As a result, one of the advantages of using the concentrated emulsion polymerization is the higher yield per unit volume. For small reaction containers, no stirring is needed during the subsequent polymerization. Since the polymerization is carried out in toluene, the solvent must be removed after

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polymerization. It is more easily removed from latexes obtained via the concentrated emulsion method than from bulk materials obtained by the solution polymerization.

In a previous paper[16], PCL/PMMA composite latexes in the form of AB networks were prepared via the concentrated emulsion method and investigated. A good combination of mechanical properties and processability was achieved. In most reported results[8,9,17,18], the main purpose of inserting comonomers into PVDC was to improve its toughness, processability and thermostability. PVDC can be toughened by copolymerization because the irregularities thus generated in the chain structure decrease its crystallinity. On the other hand, the amorphous PVDC segments produced, which are very flexible, can also toughen the incorporated foreign segments. It is therefore expected that the mechanical properties of PCL/PMMA composites prepared previously by us can be further improved by incorporating segments of VDC. Motivated by these considerations, a wide range of VDC/MMA weight ratios was investigated. The mutual toughening is expected to generate improved mechanical properties in the PCL/MMA/VDC composites.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich. Vinylidene chloride (VDC, 99%), methyl methacrylate (MMA, 99%), ethyl methacrylate (EMA, 99%) and acrylonitrile (AN, 99%) were filtered through an inhibitor removing column before use. The above four monomers will be referred to as low molecular weight (*MW*) monomers. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Polycaprolactone diol (PCL diol, *MW* = 1250, 2000; 99%), acryloyl chloride (AC, 96%), triethylamine (TEA, 99%), sodium dodecyl sulfate (SDS, 70%) and the solvents were used as received. Water was deionized and distilled.

Preparation procedure

Preparation of vinyl-terminated PCL. A solution of PCL diol in toluene (20 g per 100 ml) was introduced in a single-necked flask equipped with a magnetic stirring bar. Triethylamine (TEA) (one mole for each mole of OH groups of the dissolved PCL diol) was added to the solution. The flask was sealed with a rubber septum, and the solution subjected to magnetic stirring. Acryloyl chloride (AC) (one mole for each mole of OH groups) was introduced dropwise with a syringe through the rubber septum, at room temperature. The OH group reacted with AC as follows:

$$\mathrm{R(OH)_2 + 2Cl\text{-}CO\text{-}CH{=}CH_2}$$
$$\mathrm{\rightarrow R(O\text{-}CO\text{-}CH{=}CH_2)_2 + 2HCl}$$

The HCl molecules produced in the above reaction reacted with TEA:

$$\mathrm{HCl + N(Et)_3 \rightarrow N(Et)_3HCl}$$

and the generated quaternary ammonium salt remained suspended in the system as a white powder. Removing the white powder by filtering, a toluene solution of vinyl-terminated PCL (VTPCL) was obtained. The VTPCLs prepared from PCL diol of *MW* 1250 or 2000 will be denoted VTPCL1250 or VTPCL2000, respectively.

Concentrated emulsion polymerization. In a test tube containing a solution of VTPCL in toluene (0.2 g/ml toluene), VDC, MMA monomers in various proportions and a suitable initator (AIBN, 0.015 g/g low molecular weight monomers) were introduced. The tube was sealed with a septum and kept in a water bath at 60°C for partial polymerization. After the viscosity of the solution reached a certain level (about 4–6 h), the solution was used as the dispersed phase of a concentrated emulsion. The partial polymerization was necessary because only in this manner could the stability of the concentrated emulsion be ensured. It should not, however, be too advanced, because too high a viscosity will not allow the generation of a concentrated emulsion. To prepare a concentrated emulsion, an aqueous solution of SDS (10 wt%) was first introduced in a single-necked 100 ml flask provided with a magnetic stirring bar and sealed tightly with a rubber septum. The oxygen inside the flask was removed with a nitrogen flow. Then, the partially polymerized solution containing VTPCL and the other monomers was added dropwise, with vigorous stirring into the flask with a syringe, until the volume fraction of the SDS aqueous solution became 0.15. The whole addition process lasted about 15 min, and took place at room temperature. The gel-like concentrated emulsion thus formed was additionally stirred for 15 min under a flow of nitrogen. Then, the flask was introduced into a water bath at 60°C to carry out the copolymerization among VTPCL, VDC and MMA and the homopolymerization of VDC and MMA, which lasted 48 h. The product thus obtained was washed with methyl alcohol in an extractor for 12 h and dried in a vacuum oven for 24 h. After 48 h of polymerization, the weight of the product was 92–96% of the monomers employed.

Thermal transition determination

The thermal transitions have been measured by differential scanning calorimetry, with a Perkin-Elmer DSC instrument. Each sample was scanned twice. The first heat scanning was from −50 to 225°C. After the first scanning, the specimen was cooled quickly to below −50°C and then heated for the second time from −50 to 230°C. The heating rate was 10°C min^{-1}.

Tensile testing

The powders of the products of the concentrated emulsion polymerization were thermopressed in a Laboratory Press (Fred S. Carver Inc.) at about 150°C for 3–5 min, and then cooled to room temperature. The sheets thus obtained were cut with a die to the size required by ASTM D.638-58T. The tensile testing was conducted at room temperature with an Instron Universal Testing Instrument (model 1000). The elongation speed was 50 mm min^{-1}. The calculation of the elongation at break was based on the final and initial distance between the clappers.

Insoluble species content determination

A preweighed composite sheet prepared as for the tensile testing was immersed in cyclohexanone, which is a solvent for both VDC and MMA homopolymers as well as their copolymers, in a test tube. The latter was kept in a water bath at 60°C for 60 h. Subsequently, the swollen sheet was retrieved and dried in a vacuum oven for 48 h to remove the solvent. The ratio of the weight of the remaining sheet to that of the original sheet multipled by 100 was taken as the insoluble species content (the crosslinked part of the composite).

Elemental analysis

The elemental analysis of a few specimen was performed by Quantitative Technologies Inc., Whitehouse, NJ.

RESULTS AND DISCUSSION

Appearance of the samples

Most products of the polymerization had the appearance of a white powder. In a few samples with high VDC content, the particles were bound in lumps. After thermopressing, the samples became thin sheets with diverse transparencies, some with a yellow colour of various intensities. The appearances of the sample sheets are listed in *Tables 1* and *2*, which show that both the transparency and the colour depend on the relative proportion of VDC. The segments of VDC homopolymer can easily crystallize, because of their simple and regular chain structure $-(CH_2-CCl_2)-$. In a copolymer, even though the sequences of the comonomer do not crystallize, the VDC sequences may still crystallize to some extent[19]. If the crystallites are larger than the wavelength of light, the material will be opaque; in the opposite case, it will be transparent. In addition, the specimen probably contains a continuous phase of linear copolymers and homopolymers (if any) and a dispersed phase of AB networks. If the domain size of the network is smaller than the wavelength of light, the material will be transparent. Larger crystallites and larger network domains are expected to occur at high VDC contents. Hence, the appearance of the sample provides some information about its morphology.

Table 1 The appearance and the insoluble species content (ISC) of composites based on VTPCL1250

VDC/MMA wt ratio	Transparency[a]	Colour[a]	ISC (wt%)
VTPCL1250 = 10 wt%			
7/1	ST	LY	78.4
6/2	ST	SY	76.7
5/3	ST	SY	70.2
4/4	T	SY	64.3
3/5	T	C	58.6
2/6	T	C	53.2
1/7	T	C	44.1
VTPCL1250 = 20 wt%			
7/1	ST	LY	80.3
6/2	T	SY	76.4
5/3	T	SY	71.2
4/4	T	SY	67.7
3/5	T	C	59.4
2/6	T	C	53.6
1/7	T	C	48.2
VTPCL1250 = 30 wt%			
7/1	ST	VSY	83.5
6/2	ST	VSY	82.1
5/3	ST	VSY	80.4
4/4	T	C	76.3
3/5	T	C	71.1
2/6	T	C	64.8
1/7	T	C	53.5

[a] T, transparent; ST, semitransparent; C, clear; LY, light yellow; SY, slightly yellow; VSY, very slightly yellow

Table 2 The appearance and the insoluble species content (ISC) of composites based on VTPCL2000

VDC/MMA wt ratio	Transparency[a]	Colour[a]	ISC (wt%)
VTPCL2000 = 10 wt%			
7/1	ST	LY	76.3
6/2	T	LY	72.1
5/3	T	SY	69.6
4/4	T	SY	65.1
3/5	T	C	59.5
2/6	T	C	52.3
1/7	T	C	41.5
VTPCL2000 = 20 wt%			
7/1	ST	LY	77.8
6/2	T	SY	73.5
5/3	T	VSY	67.2
4/4	T	VSY	61.4
3/5	T	C	56.9
2/6	T	C	50.3
1/7	T	C	43.7
VTPCL2000 = 30 wt%			
7/1	ST	SY	80.1
6/2	ST	SY	78.3
5/3	T	SY	76.6
4/4	T	VSY	71.7
3/5	T	C	65.4
2/6	T	C	60.8
1/7	T	C	47.9

[a] T, transparent; ST, semitransparent; C, clear; LY, light yellow; SY, slightly yellow; VSY, very slightly yellow

The VDC segments are thermally unstable and, when heated above about 120°C, undergo dehydrochlorination to generate poly(chloroacetylene) sequences $-(CH_2CCl_2CH{=}CClCH_2CCl_2)-$ (refs 20, 21). A few local conjugate poly(chloroacetylene) sequences are enough to stain the samples with the yellow colour. We observed that the yellow colour was always associated with a high VDC content. Those with VDC/MMA weight ratios below 4/4 remained clear, even after thermopressing at 150°C for more than 20 min. It should be emphasized that the thermal stability of these samples was so high that no stabilizer was needed during thermopressing. For most of the VDC-based polymers the stabilizer was absolutely necessary[22].

Insoluble species content

The insoluble species contents (ISCs) of the samples are listed in *Tables 1* and *2*. In the ideal case, the reactants should form a complete network, which could only swell but never dissolve in any solvent. In reality, parts of the monomers VDC or MMA polymerize separately, generating linear homopolymers and copolymers. As a result, the composite is a blend of linear homo- and copolymers and one or several networks. Since the linear and the network species contribute to the mechanical properties in different ways, it is important to have information about the content of insoluble species. *Tables 1* and *2* show that the contents of both MMA and PCL, and the *MW* of the PCL, affect the ISC. The

Table 3 Chlorine content of some samples (wt%)

VDC/MMA/VTPCL2000 initial wt ratio	Cl content in initial reactant	Cl content in product by elemental analysis
6/2/2	43.9	42.47
3/5/2	22.0	24.67
1/7/2	7.3	8.70

effect of the PCL can be easily understood, since the higher the content of PCL, the higher the degree of crosslinking. For the same weight content of PCL, VTPCL1250 provides a larger number of bivinyl-terminated monomers than VTPCL2000 and hence the degree of crosslinking will be higher. The effect of the MMA content is somewhat more complex. The polymerization was carried out in a toluene solution and the mixture of toluene and MMA is a poor solvent for the MMA homopolymer and the copolymers with high MMA content. When a polymer chain with high MMA content is generated in the solution, it will separate without having the opportunity to react with the VTPCL monomers and thus to be included in the network. Consequently, the higher the MMA content, the more likely that the polymerization will be heterogeneous, since more linear species will be generated.

Elemental analysis

Three specimens were analysed for their chlorine content and the results are presented in *Table 3*, which shows that the chlorine content is very close to the initial amount introduced into the system.

Thermal transitions

From the nature of the system and the results of solubility measurement, the composites are expected to consist of an AB network, which is a combination of PCL chains and sequences of VDC and MMA, and VDC, MMA homo- and copolymers. Differential scanning calorimetry (d.s.c.) diagrams provide some information in this direction. Each of the d.s.c. diagrams exhibits a distinctive glass transition (T_g) between 19 and 60°C. Since the T_g of the amorphous PVDC is −17°C and that of PMMA is 115°C (ref. 23), it is reasonable to attribute the distinctive T_g to the AB network and to the VDC/MMA copolymers. Indeed, *Table 4* shows that T_g depends on both the VDC/MMA weight ratio and the content of PCL. The larger the contents of MMA and PCL, the higher the T_g. The increased crosslinking generated by higher contents of PCL is responsible for the higher T_g. Comparing for the same weight content the composites based on PCL2000 with those based on PCL1250, one can see that the T_gs based on PCL1250 are higher. This occurs because the shorter chain length of PCL1250 provides a higher degree of crosslinking for the same weight content. In addition, some (not all) of the d.s.c. diagrams provide a vague T_g between 110 and 115°C which indicates the presence of PMMA homopolymer, as well as a vague melting point (T_m) above 190°C which is the T_m of PVDC homopolymer. Their absence in some diagrams and vague presence in others indicate that the amount of homopolymer is small. It is likely that most of the soluble species are copolymers.

Table 4 Glass transition temperature of the composites (°C)

VDC/MMA wt ratio	PCL2000 = 10 wt%	PCL2000 = 20 wt%	PCL2000 = 30 wt%	PCL1250 = 20 wt%
7/1	–	19	–	–
5/3	18	29	45	34
3/5	33	35	52	47
1/7	–	53	–	–

Stress–strain curves

A set of typical stress–strain curves is presented in *Figure 1*. The samples have the same VTPCL2000 content (10 wt%), but various VCD/MMA weight ratios. One can see that as the MMA content increases, the material changes from soft to hard, from flexible to tough, and from tough to brittle. The seven samples represent all the types of stress–strain curves of polymer materials. Sample no. 1 is a soft elastomer. The stress increases initially with strain and becomes constant after a certain strain (50%). The stress plateau is maintained until the sample is near the breaking point. There is a small fall in stress before the latter point. No. 2 is a stiffer elastomer. The stress keeps increasing with strain till the breaking point is reached. No. 3 shows behaviour between those of a tough plastic material and an elastomer. A smeared yield point can be observed, after which the stress–strain curve becomes similar to that of No. 2. Nos 4 and 5 are tough plastics. Each of their stress–strain curves has a sharp yield point. However, No. 5 is not as tough as No. 4. The latter develops a large strain after the stress softening, whereas the former breaks during stress softening. One can consider that sample No. 6 is a leather-like material. It is not very tough nor very brittle and breaks before the yield point is reached. No. 7 is a

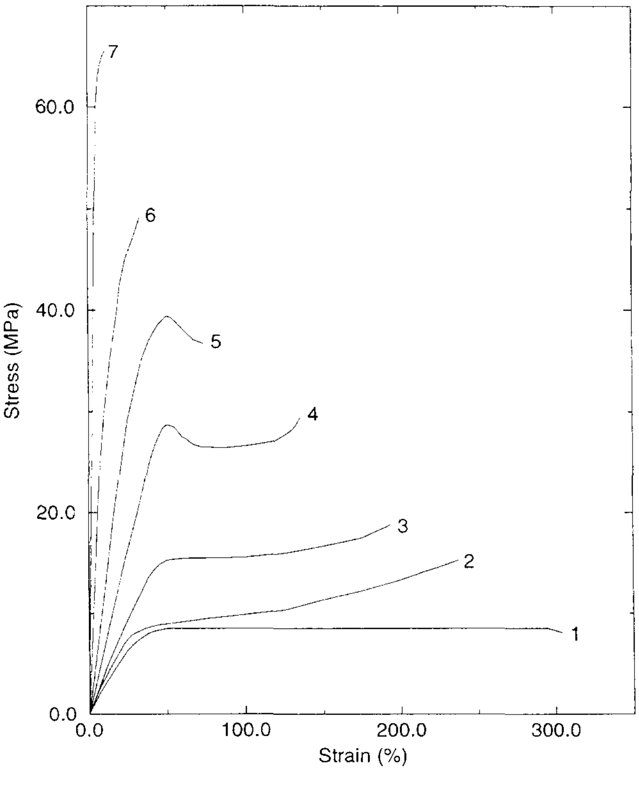

Figure 1 Stress–strain curves of the PCL/PVDC/PMMA composites VTPCL2000 = 10 wt%. VDC/MMA weight ratio: (1) 7/1; (2) 6/2; (3) 5/3; (4) 4/4; (5) 3/5; (6) 2/6; (7) 1/7

brittle plastic material with high tensile strength but very low elongation at break. The most distinctive feature of these stress–strain curves is that the yield points are located at a high strain (50%). Most plastics have a yield point at very low strain, below about 10% (ref. 24). That means that the tough materials prepared in the present work are most suitable for high impact circumstances.

Effect of VDC/MMA weight ratio on mechanical properties

The tensile strength and the elongation at break, and the toughness, which is measured by the area under the stress–strain curve, are presented in *Tables 5* and *6*. One can see that the VDC/MMA weight ratio plays a major role in these mechanical properties. When the weight ratio changes from VDC/MMA = 7/1 to 0/8, the tensile strength increases eight to 50 times, the elongation decreases six to 30 times and the toughness exhibits a maximum. It is interesting to note that the VDC and MMA components behave like mutual tougheners. PVDC, owing to its high crystallinity, is very rigid and very brittle. Once it is copolymerized with another monomer, such as MMA, the regularity of the chain structure is greatly destroyed, and the VDC segments in the copolymer chains become amorphous and behave like a rubber. As a result, the copolymer will be flexible. On the other hand, due to its highly polar lateral groups, PMMA is also a rigid and brittle polymer. The inclusion of VDC sequences, however, separates the polar groups. As the relative proportion of VDC sequences increases, the copolymer chains become increasingly more flexible. Nevertheless, if it becomes too large, the chains acquire the characteristics of the PVDC chains. In the two extreme cases, PVDC and PMMA, the materials are brittle. To be tough, a polymer material must have suitable flexible chains and suitable chain interactions. A flexibility that is too high makes the material soft while interactions among the chains that are too strong result in brittleness. A maximum in toughness located near the weight ratio of VDC/MMA = 4/4 is achieved. The flexibility of the VDC sequences and the interactions among the MMA segments provide just the right balance in the vicinity of VDC/MMA = 4/4 to lead to maximum toughness.

The data for the VDC/MMA weight ratio of 0/8 in *Tables 5* and *6* were taken from our previous paper[16]. Compared with the results of the present paper, one can see that a small amount of VDC in the system does not change appreciably the mechanical properties. However, as the content of VDC increases, the changes

Table 5 Mechanical properties of composites based on VTPCL1250

VDC/MMA wt ratio	Tensile strength (MPa)		Elongation (%)		Toughness ($MJ\,m^{-3}$)	
	Av. value	Std error	Av. value	Std error	Av. value	Std error
VTPCL1250 = 10 wt%						
7/1	7.9	0.7	292	14.8	17.5	2.5
6/2	13.8	0.9	181	7.5	19.4	0.5
5/3	17.3	1.1	132	6.9	18.6	0.6
4/4	30.4	1.9	119	4.2	32.2	0.7
3/5	42.2	2.3	69	4.0	25.1	0.7
2/6	47.7	3.1	25	1.2	10.4	0.3
1/7	63.3	2.8	9.2	0.3	4.7	0.1
VTPCL1250 = 20 wt%						
7/1	6.2	1.5	435	21.1	18.6	2.2
6/2	11.2	1.5	306	15.1	25.2	1.6
5/3	16.6	1.8	198	16.0	24.9	2.3
4/4	29.2	1.1	165	14.3	40.4	1.3
3/5	33.8	1.3	75	4.4	21.2	0.5
2/6	39.2	1.3	32	1.7	10.0	0.2
1/7	49.1	5.0	17	0.9	6.1	0.3
0/8[a]	50.7	2.7	23	2.2	7.9	1.2
VTPCL1250 = 30 wt%						
7/1	0.7	0.1	493	34.0	2.3	0.2
6/2	2.8	0.2	351	18.5	7.0	0.3
5/3	4.8	0.8	267	20.7	9.7	0.8
4/4	15.8	1.7	204	7.6	27.1	1.1
3/5	19.5	1.3	136	9.9	20.4	1.0
2/6	27.2	2.6	104	5.9	21.1	1.2
1/7	33.8	2.9	80	5.4	19.0	1.1
0/8[a]	35.7	2.3	41	3.2	10.4	1.3

[a] Data taken from ref. 16

Table 6 Mechanical properties of composites based on VTPCL2000

VDC/MMA wt ratio	Tensile strength (MPa)		Elongation (%)		Toughness (MJ m^{-3})	
	Av. value	Std error	Av. value	Std error	Av. value	Std error
VTPCL2000 = 10 wt%						
7/1	8.1	1.2	304	14.2	18.5	1.3
6/2	15.3	1.0	237	19.6	28.4	1.5
5/3	18.8	1.2	194	14.5	30.4	1.4
4/4	29.5	2.9	136	10.2	35.6	2.7
3/5	36.7	1.7	74	3.4	23.4	0.5
2/6	49.2	2.0	33	1.1	14.0	0.2
1/7	65.5	2.5	11	1.7	5.3	0.3
VTPCL2000 = 20 wt%						
7/1	7.4	0.8	527	17.5	27.8	0.4
6/2	16.6	2.2	294	28.4	36.3	0.5
5/3	18.5	1.8	241	7.5	35.1	1.1
4/4	30.4	1.7	189	8.5	47.9	0.7
3/5	32.3	5.2	96	3.1	25.2	1.3
2/6	43.6	2.4	51	3.8	18.0	0.7
1/7	57.9	3.9	40	3.4	17.4	1.0
0/8[a]	54.6	2.0	31	2.5	11.8	1.5
VTPCL2000 = 30 wt%						
7/1	1.1	0.2	758	17.3	5.0	0.2
6/2	2.7	0.5	425	18.0	9.1	0.6
5/3	5.1	1.2	315	22.3	12.0	0.7
4/4	15.2	1.3	285	9.8	36.0	1.1
3/5	21.6	0.8	188	5.6	32.7	0.4
2/6	34.0	1.8	108	1.8	27.6	0.2
1/7	39.5	2.3	42	2.1	12.1	0.4
0/8[a]	37.2	2.8	44	2.7	11.1	1.2

[a] Data taken from ref. 16

become major. We also prepared samples free of MMA (VDC/MMA weight ratio = 8/0). The VDC segments in these samples have high crystallinity and the specimens were so brittle that the testing of their tensile properties became very difficult. For this reason no data are provided for those composites.

Effect of PCL segments on mechanical properties

The effect of PCL is summarized in *Tables 5* and *6*, which show that the inclusion of PCL into the system produces two kinds of change: (i) PCL provides chemical crosslinking, in addition to the physical crosslinking already present among the VDC/MMA copolymer chains; (ii) the VDC/MMA copolymer segements are separated by flexible segments of PCL and thus additional free volume is generated. In other words, besides the role of a crosslinker, PCL also acts as a toughener, since the increased free volume results in a lower tensile strength and higher elongation at the break point. Regardless of the *MW* of PCL, the higher the PCL content, the lower the tensile strength and the higher the elongation at break. As noted in the previous section, maximum toughness can be achieved in suitable ranges of flexibility and chain interactions. The change in the PCL content changes both the flexibility (by changing the free volume) and the chain interactions (by crosslinking). With only a few exceptions, it was found that optimum toughness is achieved for PCL = 20 wt% for composites based on either PCL2000 or PCL1250. It was found that, for high VDC content (VDC/MMA = 7/1, 6/2, 5/3 wt/wt), the toughness for PCL = 10 wt% was higher than that for PCL = 30 wt%. This occurs because the latter samples already contain a sufficiently high content of flexible components, and the inclusion of excess PCL softens the materials so much that their toughness decreases. In contrast, for low VDC content (VDC/MMA = 3/5, 2/6, 1/7 wt/wt), the toughness for PCL = 30 wt% is higher than that for PCL = 10 wt%. This happens because the former systems do not contain enough flexible components and, consequently, a higher PCL amount is favourable.

The chain length (*MW*) of PCL also plays a role. As indicated by the data regarding the content of insoluble species (*Tables 1* and *2*), the samples based on PCL1250 have a higher degree of chemical crosslinking than those based on PCL2000. However, because of their shorter chain length, the samples based on PCL1250 possess a lower degree of physical crosslinking, i.e. lower entanglement. As a result, the systems based on PCL of different *MW* possess roughly the same free

Table 7 Mechanical properties of composites containing EMA

VDC/EMA wt ratio	Tensile strength (MPa)		Elongation (%)		Toughness ($MJ\,m^{-3}$)	
	Av. value	Std error	Av. value	Std error	Av. value	Std error
VTPCL2000 = 10 wt%						
7/1	12.0	0.6	193	20.3	17.4	0.9
6/2	14.8	1.3	229	19.5	26.4	2.0
4/4	22.1	1.1	150	11.4	30.3	1.1
VTPCL2000 = 20 wt%						
7/1	11.3	0.2	232	22.5	18.8	0.3
6/2	12.7	1.9	244	20.1	23.2	0.3
4/4	23.3	1.8	192	11.6	37.8	1.7
VTPCL2000 = 30 wt%						
7/1	7.6	0.7	282	10.5	14.1	0.5
6/2	4.5	0.5	325	16.9	10.4	0.6
4/4	12.8	1.4	279	8.7	31.1	1.0

volumes and chain interactions, but different segmental motions. Consequently, the samples based on PCL1250 have a comparable tensile strength to those based on PCL2000, but a somewhat lower elongation at break, hence a somewhat lower toughness.

Effect of other monomers

Two other monomers, namely ethyl methacrylate (EMA) and acrylonitrile (AN) were also employed instead of MMA or part of MMA. The mechanical properties of the composites based on EMA are presented in *Table 7*. EMA is very similar to MMA in chemical structure, but has a somewhat larger and much less polar lateral group. Because of this difference in the side groups, the composites based on EMA are expected to have a lower tensile strength and a higher elongation at break, but a comparable toughness to the samples based on MMA. This indeed happened with the composites with VDC/EMA weight ratio of 6/2 and 4/4. However, the specimens with VDC/EMA = 7/1 behaved differently. Compared with the samples based on MMA, they had a higher tensile strength and a much smaller elongation at break. We also observed that their thermopressed sheets had an opaque appearance, which was probably caused by the crystallization of VDC sequences. Because the EMA sequences are not as stiff as those of MMA, a low EMA content (such as VDC/EMA = 7/1) is not efficient enough to prevent the crystallization of the VDC sequences.

The mechanical properties of the composites containing AN are presented in *Table 8*. AN has a lateral group with a higher polarity than MMA. A higher tensile strength and a lower elongation at break are therefore expected for the samples containing AN. However, only when the AN has replaced the entire amount of MMA have such changes been observed. When AN replaced only part of MMA, the mechanical properties were comparable to those of samples based on MMA alone. A likely explanation may be as follows. The addition of the fourth monomer to the PCL/VDC/MMA system increased the randomness and irregularity of the chains. The somewhat higher polarity of the AN monomers is probably compensated by the additional free volume generated by the higher irregularity of the chain. Consequently, no major changes should occur in the mechanical properties.

CONCLUSION

The PCL/VDC/MMA network composites prepared in this paper are in reality blends containing AB networks and some linear homo- and copolymers of VDC and

Table 8 Mechanical properties of composites containing acrylonitrile (VTPCL2000 = 20 wt%)

VDC/MMA/AN wt ratio	Tensile strength (MPa)		Elongation (%)		Toughness ($MJ\,m^{-3}$)	
	Av. value	Std error	Av. value	Std error	Av. value	Std error
7/1/0	7.4	0.8	527	17.5	27.8	0.3
7/0.5/0.5	7.7	1.0	498	17.7	27.2	1.3
7/0/1	9.3	0.8	401	20.5	26.5	1.2
5/3/0	18.5	1.8	241	7.5	35.1	1.1
5/2/1	17.9	1.1	277	13.1	40.0	1.1
5/1/2	16.0	0.7	281	16.2	36.0	0.9
5/0/3	23.8	1.5	177	18.2	33.9	2.2

MMA. They possess good thermal stability, and can be melt-processed at or below 150°C without a stabilizer. Depending on the weight ratio of VDC/MMA, these composites can be either tough plastics or elastomers. PMMA and PVDC are mutual tougheners: PMMA segments toughen PVDC by decreasing its crystallinity, and amorphous PVDC segments toughen PMMA by separating its polar lateral groups. An optimum VDC/MMA weight ratio and an optimum content of PCL for the highest possible toughness were observed.

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